



Titanium dioxide photocatalysis: An assessment of the environmental compatibility for the case of the functionalization of heterocyclics

Davide Ravelli^a, Daniele Dondi^b, Maurizio Fagnoni^a, Angelo Albini^{a,*}

^a Department of Organic Chemistry, University of Pavia, via Taramelli 10, 27100 Pavia, Italy

^b Department of General Chemistry, University of Pavia, via Taramelli 10, 27100 Pavia, Italy

ARTICLE INFO

Article history:

Available online 16 May 2010

Keywords:

Photocatalysis
Titanium dioxide
Life Cycle Assessment
Environment
EATOS Assessment

ABSTRACT

The environmental burden associated with some functionalization reactions of nitrogen-heteroaromatics via TiO₂ (solar) photocatalysis is compared with the same reactions under thermal conditions. Two methods, LCA (Life Cycle Assessment) and EATOS (Environmental Assessment Tool for Organic Synthesis), both based on a detailed analysis of the experiments, are used for the assessment. The thermal processes are consistently evaluated to give a better environmental performance. Photocatalysis is disfavored by the required management of a large amount of excess reagent and solvent involved. Still the good yield and simplicity of the photocatalytic method are promising (and are positively evaluated by a third assessment, EcoScale). The precautions for making photocatalytic syntheses environmentally viable are discussed.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

It is difficult to exaggerate the importance of titanium dioxide as a photocatalytic material. Since the relatively recent (early-1970s) discover of the photoactivity of this material a rapid and sometimes tumultuous development has made this one of the most important fields of photochemistry. A variety of applications have been introduced, the main ones being depollution of water and air and photocatalytic water splitting for the generation of hydrogen [1–11], but many others being actively investigated, from disinfection to self cleaning surface [12], to the use in photodynamic therapy and many more [13]. In this connection, the inexpensive dioxide sold as pigment has been used in most cases, but a large number of ad hoc materials have been prepared and shown to be advantageous under various aspects, from extending light absorption to the visible to an enhanced activity.

An application that has been introduced relatively late involves the synthesis of fine chemicals. A number of synthetic processes has been reported, including oxidation and reduction reactions as well as carbon–carbon bond forming reactions, such as alkylations and radical coupling [14–19]. In this, as in previous instances, it is taken advantage of the ability of excited TiO₂ of generating highly reactive species, i.e. mostly organic radicals, under mild conditions. These conditions are compatible with the postulates of ‘green chemistry’ [20]. However, recognizing whether assigning this label is actually appropriate requires a more extensive examination, in order

to establish not only that this is a mild process, but also that it is actually more environment-friendly than competing methods after consideration of all of the aspects involved.

This is usually done through a Life Cycle Assessment (LCA), based on the detailed measurement of all the facets, from the production of the starting materials of the reaction under consideration, to the energy used, to the problems encountered after the reaction, such as recovering and disposing of (or reusing) the materials [21–23]. Alternatively, one may choose one of the methods developed from the original proposals by Trost and Sheldon, with the concept of ‘atom economy’ (how many atoms of the substances involved in the reaction end up in what is considered as the product and how many in ‘waste’) [24,25], or with the similar concept of ‘mass intensity’ [26]. These methods have been further developed by attaching a label qualifying the degree of environment friendliness or unfriendliness to all of the substances involved [27,28]. The LCA approach is more comprehensive and considers the energetic/engineering aspects, while the other approaches above are limited to the mere chemical characteristics.

As one may expect given the importance of the above mentioned applications, life cycle analyses have been carried out for the production of titanium dioxide itself [29] as well as for various photochemical applications that have already reached the upscaling stage, particularly depollution and disinfection [30–34]. To our knowledge, however, not for the synthesis of fine chemicals. Since this aspect has been growing during the last years, it seemed to us appropriate to apply this analysis also to this case, and to supplement it with a more ‘chemical’ assessment, which is well suited for the case of a synthesis. Furthermore, an easily determined index, EcoScale, was also calculated. As for the test reactions, for the rea-

* Corresponding author. Tel.: +39 0382 987316; fax: +29 0382 987323.
E-mail address: angelo.albini@unipv.it (A. Albini).

Table 1

Amount of chemicals and of energy used in the amidation and alkylation processes (Eqs. (1)–(4)), normalized for the synthesis of 500 mg final product(s).

Reagents/energy	Lepidine + formamide		Quinoxaline + formamide		Quinoline + diethyl ether		Quinoline + THF
Methods and chemical yields (%)	Thermal (38) ^a (1a)	Photocatalytic (69) (1b)	Thermal I (23) ^a (2a)	Thermal II (36) ^a (2b)	Photocatalytic (42) (2c)	Photocatalytic (45) (3)	Photocatalytic (75) (4)
Heteroaromatic base	980 mg	557 mg	1.66 g	1.04 g	895 mg	713 mg	432 mg
Formamide	19.3 g	176 g	36.1 g	22.5 g	311 g		
Sulphuric acid/acetic acid	671 mg	382 mg	1.25 g	1.04 g	1.35 g	322 mg	201 mg
Hydrogen peroxide		530 mg			935 mg	750 mg	455 mg
Titanium dioxide		38.9 mg			68.7 mg	52.5 mg	33.5 mg
Fe(II) sulfate	57.1 mg		106 mg	222 mg			
HSA	774 mg		1.44 g	902 mg			
Water	1.71 g		3.19 g	1.99 g		27.6 g	100 g
Heating	1.85 MJ						
Diethyl ether						39.2 g	
Acetonitrile						43.4 g	
THF							29.8 g

^a Based on total amount of chemicals used.

sons presented below, we chose some functionalization of nitrogen heterocycles as representative examples. The results of the analysis are reported below.

2. Experimental

The environmental assessment has been carried out by using the software SimaPro Version 7 (Eco-Indicator99 evaluation method) for the LCA [35] and the EATOS software [27]. The reactions considered are presented in the Results section.

The input data for reagents used and, where appropriate, the energy consumed for heating are listed in Table 1. The analysis is limited to the reaction step, excluding work up and product isolation procedure.

The results obtained are available as Supplementary Material in Table S1 for the EATOS method and in Tables S2–S5 for the life cycle analysis. Likewise, detail of the input data and results for the EcoScale assessment are reported in Table S6.

In detail, for the EATOS analysis the physical and environmental information (including risk and safety phrases, toxicity and ecological parameters) of considered compounds were obtained from the safety data sheets available on the Sigma Aldrich web site [36].

For the LCA the impact categories considered in the impact assessment were: Carcinogens, Respiratory organics, Respiratory inorganics, Climate change, Radiation, Ozone layer, Ecotoxicity, Acidification/Eutrophication, Land use, Minerals and Fossil fuels, as demanded by the method mentioned above.

The required data for the chemicals involved have been taken from the databases present in the software when available. When this is not the case, an approximation has been made, and precisely for the following compounds.

- **Formamide.** The production of this chemical has been simulated by assigning the appropriate parameters to the actual industrial process, that is based on the amonolysis of methyl formate (in turn, obtained from the carbonylation of methanol).
- **Heteroaromatic compounds.** The commercial samples of these products are obtained from the appropriate cut of the distillation of coal tar. Thus the contribution of these chemicals has been simulated by considering their source.
- **Hydroxylamine-O-sulfonic acid (HSA).** This chemical has been modeled by considering the only related redox active material present in the database, viz. hydrogen peroxide.
- **Trifluoroacetic acid.** Some of the process uses this acid agent, not present in the database. In the analysis this has been substituted by acetic acid.

- **The energy consumption** (Italian mix, medium voltage) has been evaluated on the base of actual experiments performed in the author's laboratory.

3. Results

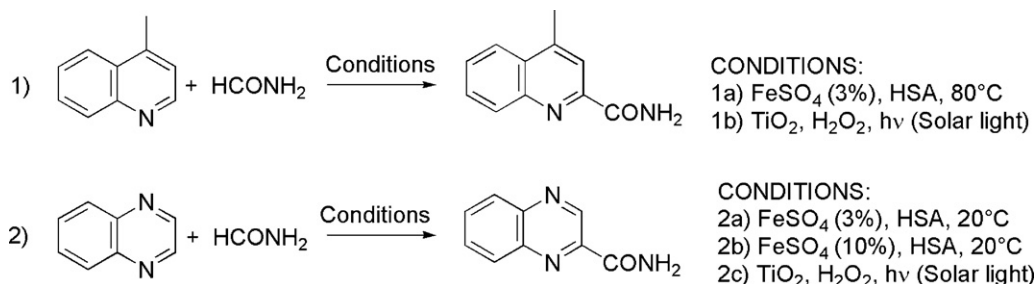
3.1. Reactions chosen

The largest number of titanium dioxide photocatalyzed syntheses involves controlled oxidation (mostly oxygenation) and reduction processes. In that case, however, a partial (often low) conversion is obtained. This is appropriate for large scale production, but requires for the environmental evaluation that recover and reuse of the starting material are considered. Therefore, it would be difficult to compare photocatalytic and thermal processes, because the latter ones have already been studied in more detail and have been upscaled, so that conditions are not comparable. More reasonable, and more close to our interest, is considering a carbon–carbon bond forming reaction, where it is more likely that small scale, niche productions become competitive and where photocatalytic methods can more easily be compared with different methods. After consideration of various possibilities (reviews of preparative photocatalyzed syntheses are available) [14–19], we pointed our attention onto the alkylation and amidation of nitrogen heterocycles under acidic conditions. These are radical processes that are typical of the chemistry via TiO₂ photocatalysis as it is presently known and find a close parallel in thermal methods of radical generation.

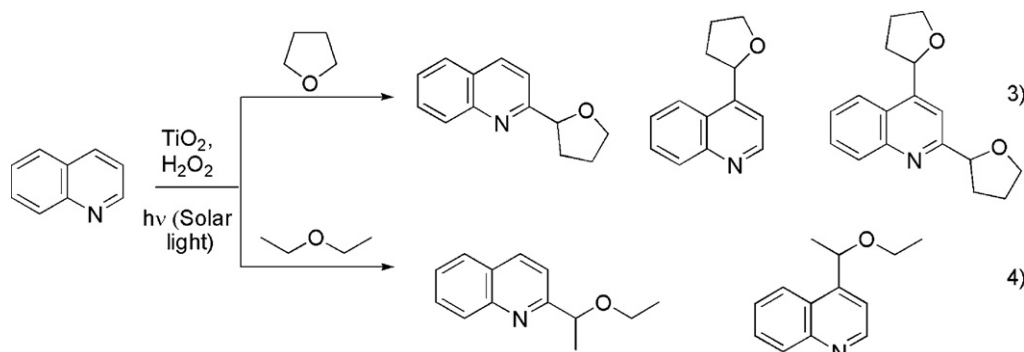
In particular, we considered the amidation and the alkoxyalkylation of quinolines and quinoxaline in acids. The amidation has been reported by Citterio et al. under thermal conditions and involves the use of hydroxylamine-O-sulfonic acid (HSA) and a Fe(II) salt in 0.36 M solutions of the heterocycles in formamide/water 10/1 (v/v) solution, as shown below. The functionalization of lepidine has been obtained at 80 °C in the presence of 3% equiv. FeSO₄ (yield 38%, see Eq. (1a)) and that of quinoxaline at 20 °C in the presence of either 3% or 10% FeSO₄ (yield 23 and 36%, respectively, see Eqs. (2a,b)) [37] (Scheme 1).

The same products have been obtained by photocatalysis, based on the use of titanium dioxide and solar radiation in the presence of hydrogen peroxide (4 equiv.), as reported by Caronna et al. for lepidine (see Eq. (1b)) and quinoxaline (see Eq. (2c)). The reactions have been carried out on 0.025 M solutions of the heterocycles in neat formamide [38].

Furthermore, the approach has some generality. Thus, both simple and functionalized alkyl groups can be introduced via related C-centered radicals, under both thermal and photocatalytic condi-



Scheme 1. Thermal and photocatalytic amidation of some heterocycles.



Scheme 2. Photocatalytic alkylation of quinoline.

tions [37]. As an example, α -alkoxyalkyl radicals generated from ethers can be used for the functionalization of this kind of heterocycles. Thus, quinoline (0.04 M) has been alkylated (45% yield, mixture of 2- and 4-alkyl derivatives) by exposing to sunlight a solution in 2/2/1 ether/acetonitrile/water containing 4 equiv. H₂O₂ and suspended TiO₂ (see Eq. (3)). The analogous reaction with a 0.025 M in 1/3 THF/water solution gave 75% of the mixed alkylated products (see Eq. (4)) [39]. This procedure has been deemed ‘simpler and more environment-friendly for the conditions used and the amount of chemicals employed’ [39] with respect to alkylation reaction with thermal generation of the radicals [37] (Scheme 2).

The environmental impact of competitive thermal and photochemical approaches for the preparation of such compounds has been examined, as reported below. For the sake of simplicity, the environmental analysis of such processes has addressed the reaction, excluding work-up and product isolation. In all of the reactions considered, such steps have been carried out under closely similar conditions and are not expected to introduce a difference in the ranking (see further below).

3.2. EATOS analysis

Among the methods based on atom economy and the environmental quality of chemicals used and produced we chose the EATOS (Environmental Assessment Tool for Organic Syntheses) developed by Eissen and Metzger [27]. This takes into account a reasonably large number of characteristics—that are easily found in public databases, though, and thus can be carried out without major stumbling blocks and gives sensible estimates. Indeed, the method has been used with satisfactory results for a variety of reactions, including photochemical examples [40]. The program evaluates the chemical processes through four indices that are referred to the *quantity* of the chemicals used (the mass index ΣS^{-1}) and discarded (the environmental factor ΣE) and respectively to the corresponding *quality* ($\Sigma E_{in} = \Sigma S^{-1} \times Q_{in}$, $\Sigma E_{out} = \Sigma E \times Q_{out}$) where the above indices are multiplied by an appropriate quality factor Q . All input/output chemicals are taken into account (substrates,

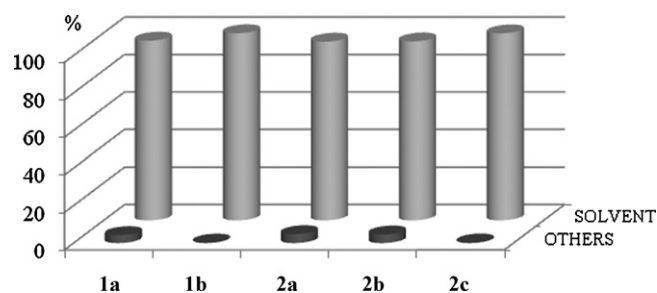


Fig. 1. EATOS analysis: breakdown (%) of the main contributions to the environmental impact of reactions in Eqs. (1a)–(2c).

solvents, catalysts, by-products and coupled products)¹ and thus the environmental and social cost involved (considered in factor Q), but not the energy used in the process.

The analysis has been applied to the amidation of lepidine and quinoxaline by thermal reaction with HSA and by TiO₂ photocatalysis as indicated above. The system is automatically adjusted by the software to the synthesis of 1 kg of product. The parameters obtained for the above reactions are reported in the Supplementary Material in Table S1. The E_{out} values, probably the most significant ones because they give an immediate idea of the environmental burden associated with the synthesis, range from 250 to 460 PEI (Potential Environmental Impact)/kilogram for the thermal reactions. These values are much higher (that is, the environmental performance is worse), however, for the photochemical activation (2100 PEI/kg for process (1b), 3700 for (2c), see below Fig. 6 for a graphical comparison).

The conditions of the experiment contribute to a different degree to this result. In Fig. 1, the E_{out} data are normalized and split in two parts, viz. excess reagent/solvent on one hand, and

¹ Coupled products are the chemicals different from what can be sold, coupled with it in the stoichiometric equation.

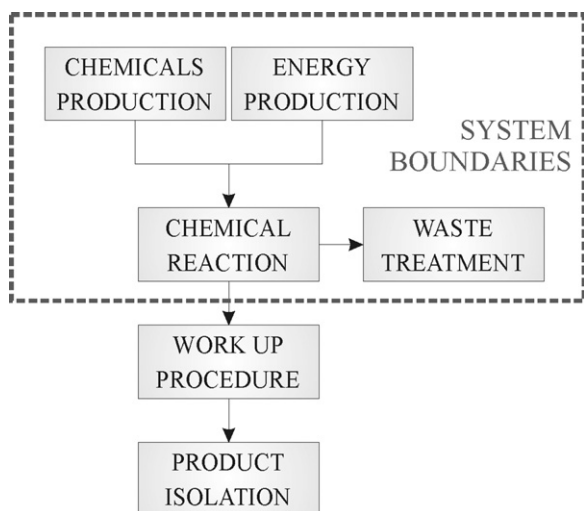


Fig. 2. Flow diagram for a chemical reaction and boundaries considered for the Life Cycle Assessment.

other contributions (substrates, solvents, catalysts, by-products and coupled products) on the other one. This partition evidences the overwhelming contribution of the solvent to the environmental impact (ca. 95% in thermal cases, >99% in photocatalytic reactions). In fact, formamide is used in excess in Eqs. (1a), (2a,b) (the analysis considers it as a solvent), neat in Eqs. (1b), (2c).

The above results refer to the case where all of the materials entering the reaction are 100% consumed. Clearly, in the ideal case where the solvent would be fully recovered, all of the indices would thus drop by (up to) one to two orders of magnitude. In order to fully address this issue, however, a different analysis would be required for the determination of how financially and environmentally expensive would be such procedures.

3.3. Life Cycle Assessment

The more complete approach of the LCA was next applied to the same processes. Besides the overall ranking, the LCA procedure allows to evaluate separately the most environmental hazardous aspects of the chemical processes considered. Four basic stages have been considered, viz. (1) goal and scope definition, where the purpose of the procedure, the boundaries of the system and the quality of the data have been indicated; (2) inventory analysis, in which data have been collected in order to quantify the flows inside and outside the system; (3) impact assessment, where the potential environmental effects produced by the system under study have been identified and characterized, and (4) interpretation, in which the results obtained have been discussed in terms of possible ways to improve the 'greenness' of the chemical processes investigated. Fig. 2 shows the flow diagram for the whole analysis and the boundaries considered.

The processes included within the boundaries are as follows. (i) The production of all the chemicals used in the reactions involved. Consumption of raw materials and energy are taken into account, but work-up and purification procedures have been excluded, since these are similar in the methods considered. Therefore, their environmental impact is neglected at this stage of evaluation (although these would become important, were the industrialization of the process considered, including the degree of conversion). (ii) The production of energy and (iii) the incineration of the spent chemicals used in the reactions (excluded the final product, which can be conveniently used for the planned application). From these input values and using the data sources detailed in Table 1 in the Experimental, the environmental burdens associated

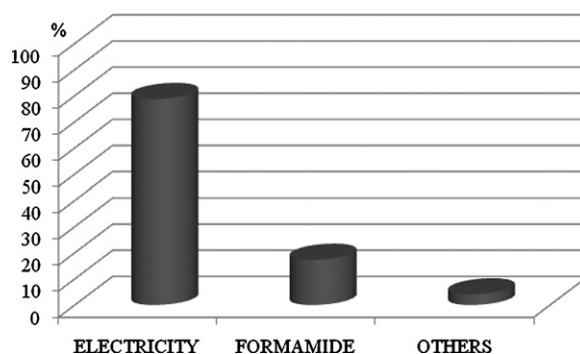


Fig. 3. LCA: breakdown (%) of the main contributions to the environmental impact of reaction in Eq. (1a).

to the product system per functional unit have been inventoried.

In the case where it is relevant (reaction (1a)) the amount of energy consumed for maintaining the temperature at 80 °C has been measured on a small scale (500 mg of end product) and the function of the system has thus been set in a broad sense as 'the synthesis of 500 mg of functionalized heteroaromatic base'.

The assessment (the lower is the number of points – pt – the better is the environmental performance, small values are obtained because of the 500 mg scale) shows again a better environmental performance for thermal reactions ($0.67\text{--}2.7 \times 10^{-2}$ pt) than for their photochemical counterpart ($4.8\text{--}8.4 \times 10^{-2}$ pt, see Table S2 in the Supplementary Material, see below a graphical representation in Fig. 6).

The factors causing the largest environmental impact have been analyzed also with this method. In the case of reaction (1a), the largest contribution comes from the electric power consumed to heat the reaction mixture to 80 °C for 2 h, while the second is due to the use of excess formamide, accounting for ca. 15% overall value (see Table S3 and histograms in Fig. 3).

On the other hand, in photocatalytic reactions, the largest contribution is given by the use of formamide (in this case used neat) and the cost associated to its disposal (see Table S4 and Fig. 4 for Eq. (1b), quite similar results for Eq. (2c), not shown).

The thermal functionalization of quinoxaline, which is carried out at 20 °C, is analyzed in Table S5 and Fig. 5 for the case of Eq. (2a) (quite similar results for (2b)). No heating is required in this case and the main contribution is given by the excess reagent.

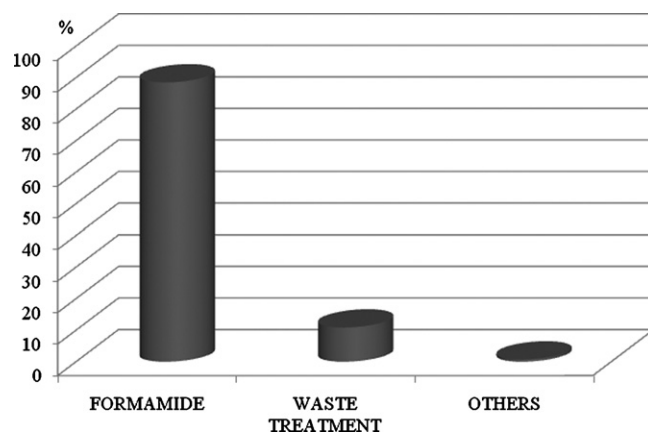


Fig. 4. LCA: breakdown (%) of the main contributions to the environmental impact of reaction in Eq. (1b).

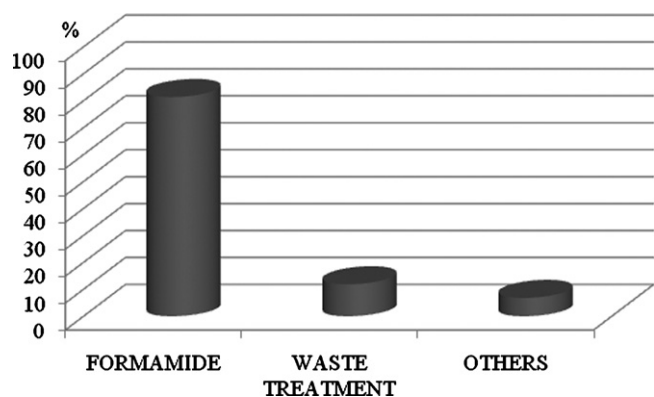


Fig. 5. LCA: breakdown (%) of the main contributions to the environmental impact of reaction in Eq. (2a).

3.4. Comparison of the assessment by different methods

The overall environmental burdens for the reactions in Eqs. (1) and (2), as evaluated by the EATOS and the LCA analysis is reported in Fig. 6, normalized to the highest value obtained for either method. Noteworthy is the close parallelism between the two different analyses, which is apparent through the comparison of the two rows in Fig. 6, with the exception of reaction 1a, where the energy contribution required by heating increases the LCA value.

It is apparent that the thermal syntheses are less impacting than the photocatalytic ones by a factor of 12–15 (See Tables S1 and S2). Breaking down to the single contributions (Figs. 1 and 3–5) show that this is due to the fact that photocatalytic reactions are carried out under diluted conditions (*ca.* 15 times more diluted than the thermal reactions).

The heavy disadvantage due to the use of a large volume of solvent in photocatalytic reaction can be at least partially obviated for by either using more concentrated solutions (see below) or by adding a less environmental unfriendly cosolvent, such as water. This is the case for the alkylations in mixed aqueous solvent in Eqs. (3) and (4) that give a much better environmental performance, as shown by the comparison of reactions (3) and (4) with the previous photocatalytic processes (1b) and (2c) (see Fig. 7, values again normalized as in Fig. 6). Obviously, the assessment is qualitative, because only reactions which give exactly the same product can be quantitatively compared, but the good performance of (3) and (4) with respect to (1b) (similar starting concentration and same mass of product obtained) is telling.

3.5. EcoScale

Van Aken et al. proposed a much simpler method that can be used for a fast comparison of different synthetic alternatives. This

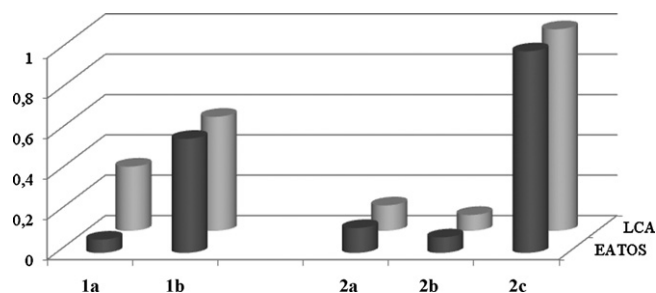


Fig. 6. Comparison of the overall environmental impact of reactions in Eqs. (1a)–(2c), according to LCA and EATOS approach, normalized to the highest value observed in either method.

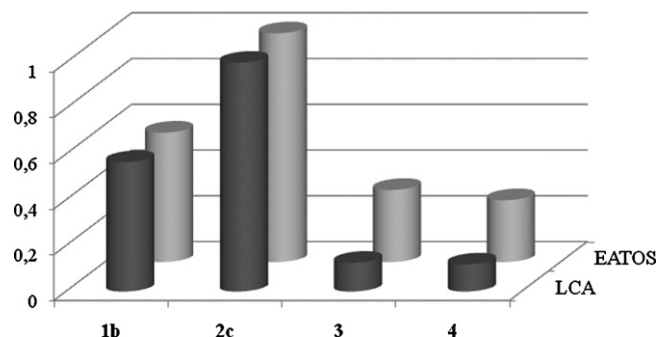


Fig. 7. Comparison of the overall environmental impact of photocatalytic reactions in Eqs. (1b), (2c), (3) and (4), according to LCA and EATOS approach, normalized to the highest value observed in either method.

is based on the yield and on a range of ‘penalties’ referred to price of reagents, safety, technical setup (a photochemical step is considered unconventional and receives a penalty), temperature/time, workup and purification (the last two items not considered in this, as in the previous cases) [41]. The values obtained are reported in Table 2 (an ideal reaction has an EcoScale value of 100).

All of the reactions rank ‘acceptable’ (>50), with Eq. (4) arriving at excellent (>75). In this approach, the dominating factor is chemical yield, unless very unsafe reagents and conditions are used (e.g. Eq. (3) suffers from a high ‘penalty’ due to the use of acetonitrile and diethyl ether). Thus, photocatalyzed reactions with their high yield perform relatively well (notice that in thermal reactions the conversion is partial), despite the 2 penalty points assigned to reactions requiring photochemical (=unconventional) activation.

4. Discussion

Using either LCA or EATOS results in a similar assessment, despite the largely different approach of the two methods. To our knowledge, such a comparison has not been previously made and the similarity of the outcome may be useful for future work, because LCA is more complete, but its implementation requires data that are available only for a few (the most largely used) chemicals. In other cases one has to resort, as we did, to approximations. On the other hand, EATOS requires data that are necessarily available from the safety profile of any commercialized product and thus are much more largely available. The actual difference is the fact that EATOS disregards the amount of energy consumed and thus is inadequate when this gives a major contribution (in the present work, this leads to the only loss of parallelism, Eq. (1a) in Fig. 6).

The above results evidence that although light, and in particular solar light, is the perfect ‘green’ reagent, the environmental assessment is not uniformly positive. Indeed, light effectively promotes chemical reactions and leaves no residue to be disposed of, contrary to the case of a chemical activating agent, but attention must be given to other factors. The dilute conditions under which a photochemical reaction is usually carried out have a negative impact on the environmental performance and this may displace the balance towards thermal methods. Such conditions are adopted in order to ensure a uniform irradiation of the solution. It would appear, therefore, that photochemical reactions are a sensible choice only when an efficient and inexpensive way for the isolation of the product (e.g. separation of a precipitate) or the

Table 2
EcoScale ranking for reactions in Eqs. (1a)–(4).

(1a)	(1b)	(2a)	(2b)	(2c)	(3)	(4)
60	71.5	51.5	61	58	51.5	79.5

recover and reuse of a considerable amount of solvent is possible.

Alternatively, one may act on either the quality or the quantity of the solvent. This means either using, where possible, an environment-friendly solvent such as water, or using a more concentrated solution. The first approach is illustrated in reactions (3) and (4), the latter one is not possible in a normal reactor with a relatively long (>1 cm) optical path, but is a viable solution in microreactors that indeed have begun to be used with considerable advantage [42]. Another way is using a membrane reactor [43]. Furthermore, in photocatalytic reactions it is the catalyst that has to be excited and this is obviously used at a much lower concentration than the reagent. Indeed, recently it has been found that a transparent reagent can be used in a concentration much larger than usual in photocatalytic reactions [44]. This could be transferred with some difficulty to the case at hand, because the heterocycles used absorb considerably up to 370 nm, leaving only the red-edge of the TiO₂ absorption free in correspondence to the fraction of UV light present in the solar spectrum.

In this way, one may take full advantage of the environmental potential of solar light driven photocatalysis, where any supply of external energy is avoided (except for stirring).

Notice further the good performance of photocatalytic reactions in the EcoScale assessment that is primarily based on the better chemical yields. The good mark in this classification evidences the present photoreactions, being 'clean' processes and involving a very simple setup (exposure to solar light in a test tube), are susceptible of improvement, possibly more than the thermal ones. The simplicity is the authentic plus of (solar) photochemical reactions, supporting the contention that photochemistry offers a significant synthetic alternative, provided that attention to the points mentioned above is given.

5. Conclusion

In the above work, three approaches to the environmental analysis of chemical reactions have been applied to some functionalization reactions of heteroaromatic compounds by thermal vs. photochemical activation. A caveat about the non-necessarily better environmental performance of photocatalytic syntheses has been formulated (indeed photocatalytic depollution too does not always give better performances than thermal methods) [30,31].

Two conclusions seem relevant, viz. the parallelism between EATOS and LCA and the key question of concentration in photochemical processes. Anybody wishing to develop a green synthetic method involving a photochemical step (that may well have a good yield, see the EcoScale assessment) should consider this point as early as possible. This conforms to the spirit of the postulates of green chemistry that demand that consideration of environmental impact accompany the development of a synthetic method, rather than being attached afterwards. With this precaution, photocatalysis should acquire a significant role in synthesis.

Supplementary material

Details of the results obtained in the environmental assessment of the reactions reported in the manuscript by different methods (LCA, EATOS, EcoScale) are enclosed as Supplementary Material.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2010.05.010.

References

- [1] A. Fujishima, K. Honda, *Nature* 238 (1972) 37.
- [2] J.A. Turner, *Science* 305 (2004) 972.
- [3] N. Serpone, E. Pelizzetti, *Photocatalysis: Fundamentals and Application*, Wiley-Interscience, New York, 1989.
- [4] M. Anpo, *Pure Appl. Chem.* (2000) 1265.
- [5] P. Pichat, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, Wiley-VCH, 1997, pp. 2111–2122.
- [6] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [7] A. Mills, J. Wang, D.F. Ollis, *J. Phys. Chem. B* 110 (1996) 14386.
- [8] S. Malato, P. Fernandez-Ibanez, M.I. Maldonado, J. Blanco, W. Gernjak, *Catal. Today* 147 (2009) 1.
- [9] W. Ren, Z. Ai, F. Jia, L. Zhang, X. Fan, Z. Zou, *Appl. Catal. B: Environ.* 69 (2007) 138.
- [10] K. Maeda, K. Domen, *J. Phys. Chem. C* 111 (2007) 7851.
- [11] A.J. Esswein, D.G. Nocera, *Chem. Rev.* 107 (2007) 4022.
- [12] N.S. Allen, M. Edge, J. Verran, J. Stratton, J. Maltby, C. Bygott, *Polym. Degrad. Stab.* 93 (2008) 1632.
- [13] E.A. Rozhkova, I. Ulasov, B. Lai, N.M. Dimitrijevic, M. Lesniak, T. Rajh, *Nano Lett.* 9 (2009) 3337.
- [14] H. Kisch, *J. Prakt. Chem.* 336 (1994) 635.
- [15] Y. Shiraishi, T. Hirai, *J. Photochem. Photobiol. C* 9 (2008) 157.
- [16] M. Fagnoni, D. Dondi, D. Ravelli, A. Albini, *Chem. Rev.* 107 (2007) 2725.
- [17] D. Ravelli, D. Dondi, M. Fagnoni, A. Albini, *Chem. Soc. Rev.* 38 (2009) 1999.
- [18] G. Palmisano, V. Augugliaro, M. Pagliaro, L. Palmisano, *Chem. Commun.* (2007) 3425.
- [19] M. Hopfner, H. Weiss, D. Meissner, F.W. Heinemann, H. Kisch, *Photochem. Photobiol. Sci.* (2002) 696.
- [20] P.T. Anastas, J. Warner, *Green Chemistry. Theory and Practice*, Oxford University Press, New York, 1988.
- [21] Center for Chemical Process Safety, USA, *Inherently Safer Chemical Processes: a Life Cycle Approach*, 2nd Ed., John Wiley & Sons, Hoboken, NJ, 2009.
- [22] P.T. Anastas, R.L. Lankey, *Green Chem.* 2 (2) (2000) 289.
- [23] M. Herrchen, W. Klein, *Pure Appl. Chem.* 72 (2000) 1247.
- [24] B.M. Trost, *Science* 254 (1991) 1471.
- [25] R.A. Sheldon, *Chem. Ind. (Lond.)* (1992) 903.
- [26] A.D. Curzons, D.J.C. Constable, D.N. Mortimer, V.L. Cunningham, *Green Chem.* 3 (2001) 1; T. Hudlicky, D.A. Frey, L. Koronik, C.D. Claeboe, L.E. Brammer Jr., *Green Chem.* 1 (1999) 57.
- [27] M. Eissen, J. Metzger, *Chem. Eur. J.* 8 (2002) 3581.
- [28] K. Hungerbühler, *Ind. Eng. Chem. Res.* 37 (1999) 3395.
- [29] E. Reck, M. Richards, *Pigm. Res. Technol.* 28 (1999) 149.
- [30] I. Muñoz, J. Rieradevall, F. Torrades, J. Peral, X. Domenech, *Sol. Energy* 79 (2005) 369.
- [31] I. Muñoz, J. Rieradevall, F. Torrades, J. Peral, X. Domenech, *Chemosphere* 62 (2006) 9.
- [32] I. Muñoz, J. Peral, J.A. Ayllón, S. Malato, P. Passarinho, X. Domenech, *Water Res.* 40 (2006) 3533.
- [33] M.J. Farré, M.I. Maldonado, W. Gernjak, I. Oller, S. Malato, X. Domenech, J. Peral, *Chemosphere* 72 (2008) 622.
- [34] J. Zhou, F. Montalto, Z.K. Erdal, P.T. McCrenan, T. Philip, *Water Environ. Res.* 81 (2009) 1451.
- [35] International Standardisation Organisation (ISO), 1997. ISO 14040: environmental management – life cycle assessment – principles and framework, Geneva, Switzerland. For the application, see: <http://www.pre.nl/simapro/>.
- [36] <http://www.sigma-aldrich.com>.
- [37] A. Citterio, A. Gentile, F. Minisci, M. Serravalle, S. Ventura, *J. Org. Chem.* 49 (1984) 3364.
- [38] T. Caronna, C. Gambarotti, L. Palmisano, C. Punta, F. Recupero, *Chem. Commun.* (2003) 2350.
- [39] T. Caronna, C. Gambarotti, L. Palmisano, C. Punta, F. Recupero, *J. Photochem. Photobiol. A* 171 (2005) 237.
- [40] S. Protti, D. Dondi, M. Fagnoni, A. Albini, *Green Chem.* 11 (2009) 239.
- [41] K. Van Aken, L. Strekowski, L. Patiny, *Beilstein J. Org. Chem.* 2 (2006), doi:10.1186/1860-5397-2-3.
- [42] E.E. Coyle, M. Oelgemöller, *Photochem. Photobiol. Sci.* 7 (2008) 1313.
- [43] V.M. Kochkodan, E.A. Rolya, V.V. Goncharuk, *J. Water Chem. Technol.* 31 (2009) 227.
- [44] S. Protti, D. Ravelli, M. Fagnoni, A. Albini, *Chem. Commun.* (2009) 7351.